Reactions of Aromatic Compounds
4 - Phenols

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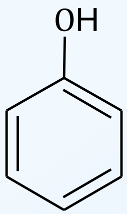
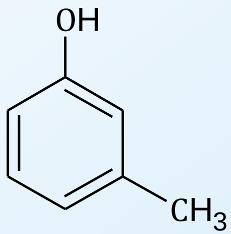
Nomenclature

Benzene with one alcohol (OH) group is called phenol. There can be one alcohol group or two or more. The diols can be ortho, meta and para – all have common names because the diols are common occurring compounds.

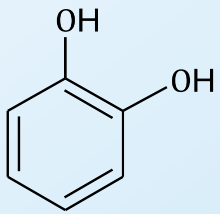


Phenol



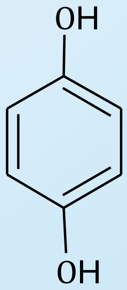
3-methylphenol

(m-cresol)



1,2-benzenediol

(catechol)



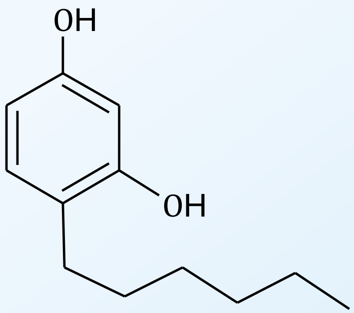
1,4-benzendiol

(hydroquinone)

Where are Phenols Found?

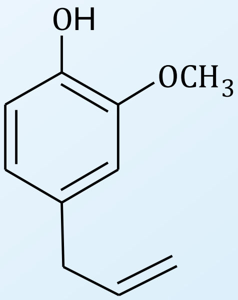
Phenolic groups are commonly found in many natural products, some examples are given below.

Hexylresorcinol



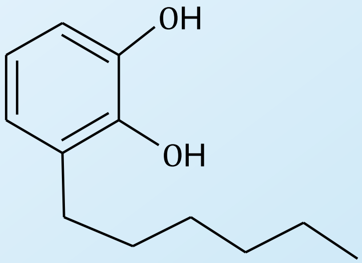
Hexylresorcinol is a mild antiseptic and disinfectant.

Eugenol



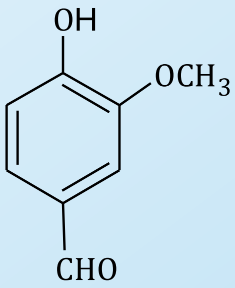
Eugenol is used as a dental antiseptic and analgesic.

Urushiol



Urushiol is the main component of the oil of poison ivy.

Vanillin



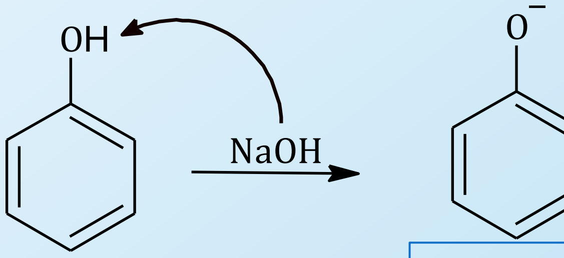
Vanillin is the most common commercial flavor.

Acidic Property of Phenols

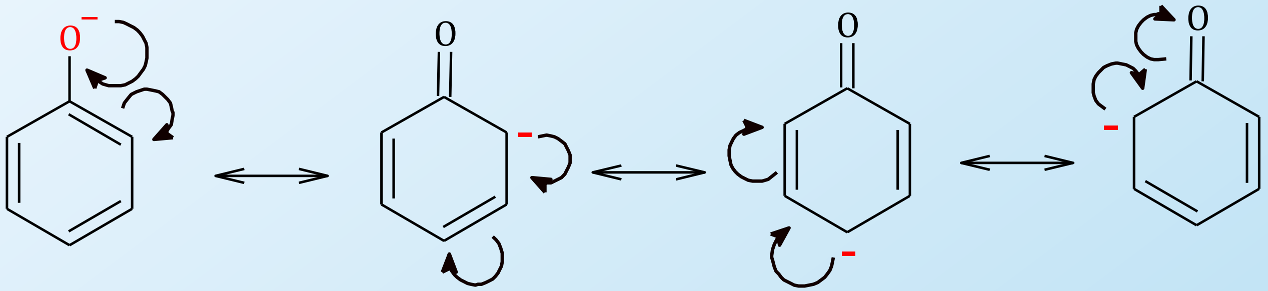
Acid	pKa
CH_3COOH	4.76
C_6H_5OH	9.89
H_2O	15.74
CH_3CH_2OH	16.00

Phenols (pK_a ~10) are much more acidic than alcohols (pK_a ~ 16) because of resonance stabilization of the phenoxide ion, shown below. Hence phenols react more readily with NaOH than aliphatic alcohols. The resonance structures are shown below.

A phenolic component can be separated from an organic solution by extraction into basic aqueous solution and is isolated after acid is added to the solution.

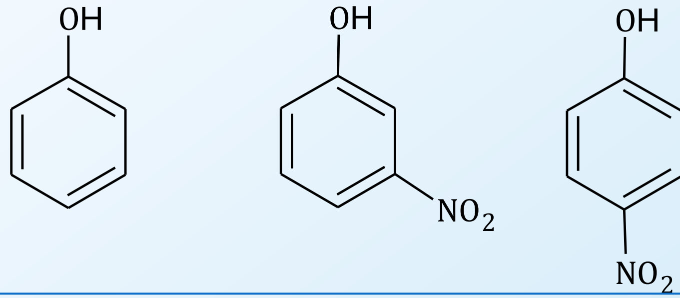


Phenoxide



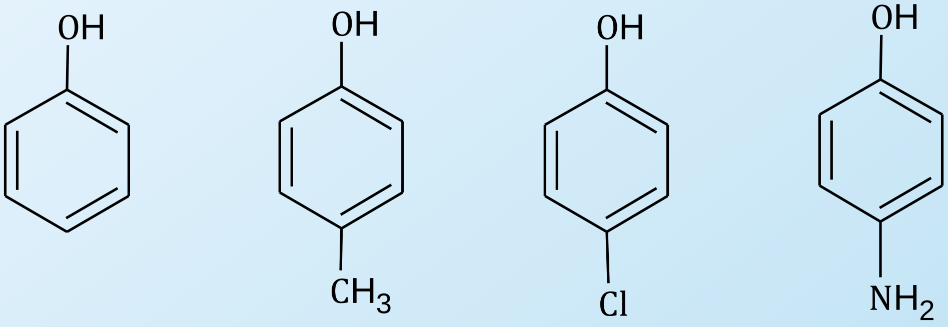
Acidity of Substituted Phenols

- Phenols with nitro groups at the *ortho* and *para* positions are much stronger acids because they are electron withdrawing groups and the inductive effect makes is easier for phenolic H to leave.



pk_a	9.95	8.78	7.15

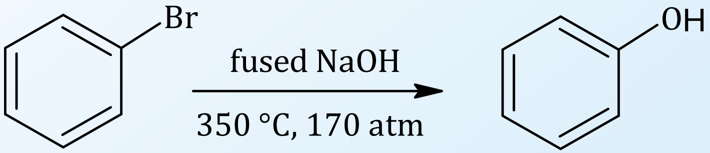
- Alkyl and halogen substituents effect acidities by inductive effects: alkyl groups are electron-releasing while halogens are electron-withdrawing.



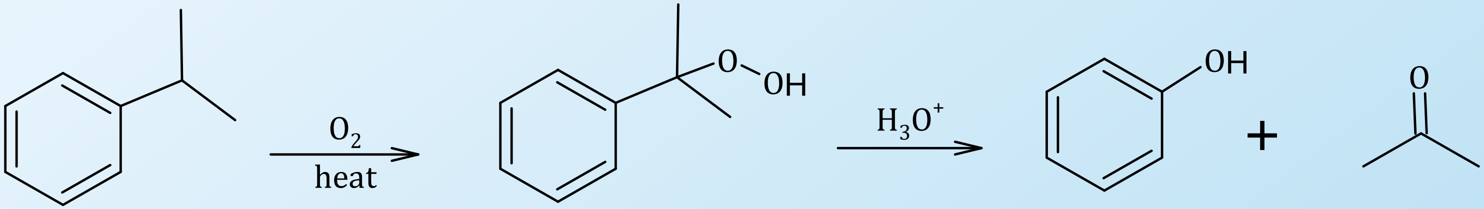
pk_a	9.95	10.17	9.39	10.46

Synthesis of Phenol

The synthesis learned so far has been the S_N2 substitution on bromobenzene using NaOH at very high temperature and pressure. These are not the best conditions to be carried out in lab. We will learn more synthesis in the amines chapter.



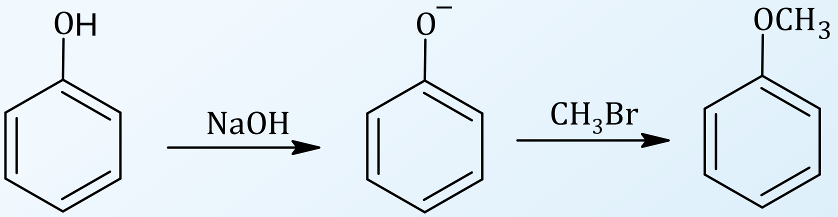
Industrial process of making phenol is from the readily available isopropyl benzene (cumene). Cumene is treated with oxygen under high temperatures to form cumene hydroperoxide. The peroxide is then hydrolysed to form phenol and acetone, both commercial products.



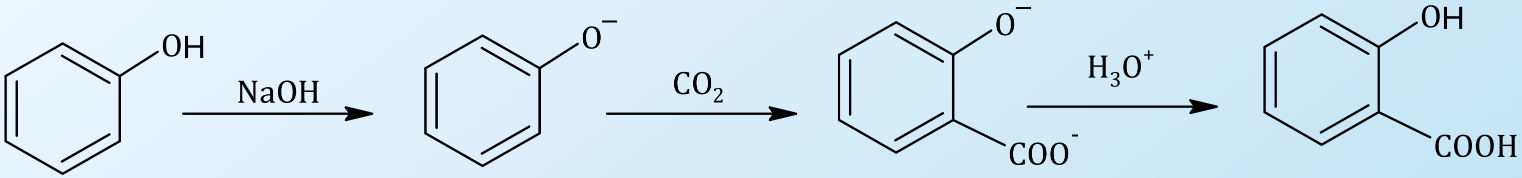
Cumene cumene hydroperoxide phenol acetone

Reactions of Phenols

Ethers: Phenols will form ethers just like alcohols through Williamson synthesis.

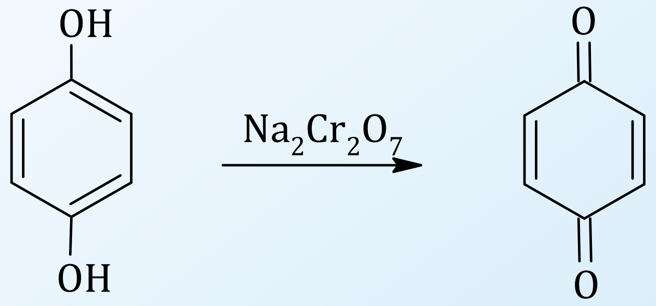


Kolbe Synthesis: Phenol is treated with NaOH to make phenoxide making the benzene ring highly nucleophilic. Addition of CO_2 to phenoxide gives substitution at the ortho position to form salicylic acid. Salicylic acid is the precursor for making aspirin, one of the most common medicine.

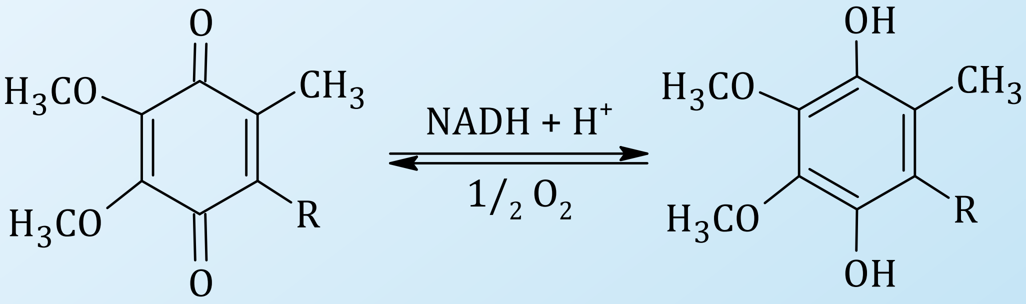


Oxidation of Phenol

1,4-Dihydroxy benzene (hydroquinone) is easily oxidized to give quinone. Quinones are a key component of the electron transport chain in nature during biochemical processes.



Ubiquinones mediate electron-transfer processes involved in energy production through their redox reaction.



Key Concepts

- Nomenclature
- Acidity of phenols
- Ether synthesis
- Kolbe synthesis
- Oxidation of diphenols